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## Short Communication

# Role of Brønsted acid in selective production of furfural in biomass pyrolysis



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## HIGHLIGHTS

- Brønsted acid enhanced the depolymerization of anhydro-oligosaccharides.
- The pyrolysis of bagasse over CuSO<sub>4</sub>/HZSM-5 obtains high furfural yield (28%).
- Py-IR identified CuSO<sub>4</sub>/HZSM-5 owned a stronger Brønsted acidity.

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## ABSTRACT

In this work, the role of Brønsted acid for furfural production in biomass pyrolysis on supported sulfates catalysts was investigated. The introduction of Brønsted acid was shown to improve the degradation of polysaccharides to intermediates for furfural, which did not work well when only Lewis acids were used in the process. Experimental results showed that CuSO<sub>4</sub>/HZSM-5 catalyst exhibited the best performance for furfural (28% yield), which was much higher than individual HZSM-5 (5%) and CuSO<sub>4</sub> (6%). The optimum reaction conditions called for the mass ratio of CuSO<sub>4</sub>/HZSM-5 to be 0.4 and the catalyst/biomass mass ratio to be 0.5. The recycled catalyst exhibited low productivity (9%). Analysis of the catalysts by Py-IR revealed that the CuSO<sub>4</sub>/HZSM-5 owned a stronger Brønsted acid intensity than HZSM-5 or the recycled CuSO<sub>4</sub>/HZSM-5. Therefore, the existence of Brønsted acid is necessary to achieve a more productive degradation of biomass for furfural.

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## 1. Introduction

As a promising BTL (biomass-to-liquid) technology, pyrolysis is widely used to produce various fuels and chemicals (Bridgwater and Peacocke, 2000; Vispute et al., 2010; Carlson et al., 2008). Bio-oil, a general term of biomass pyrolysis products, cannot be directly utilized as a fuel due to its high oxygen content, thermal instability and corrosiveness (Huber et al., 2007; Peng et al., 2009). As an important platform chemical, furfural is a significant component of bio-oil and widely applied in the manufacture of medicines, resins, food additives, fuel additives and other special chemicals (Lu et al., 2011a,b). Currently, depolymerization and degradation of biomass by acid catalysis has been the most popular approach in furfural preparation. Furfural is commercially produced from pentosan-rich biomass. In the presence of a homogeneous Brønsted acid catalyst (H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub>), pentosan can be hydrolyzed to pentose, which is then dehydrated into furfural

(Xing et al., 2011; Agirrezabal-Telleria et al., 2011). However, large quantities of corrosive wastewater is produced during this process which adds to the difficulty and expense of this method.

Consequently, selective pyrolysis for the generation of furfural has aroused increasing attention. In furfural production from biomass catalytic pyrolysis, Lewis acid catalysts have been intensively employed. For instance, ZnCl<sub>2</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> were investigated as the most promising catalysts (Oh et al., 2013; Lu et al., 2011a,b; Branca et al., 2012; Chen et al., 2008). Furfural was obtained as the major product in pyrolysis of corncob when ZnCl<sub>2</sub> was employed (Lu et al., 2011a). However, it was found that some high boiling components in this process were not completely cracked. Recently, Leng et al. obtained a higher furfural yield when using ZnCl<sub>2</sub>/HZSM-5 in the pyrolysis of bagasse, and the excellent catalytic property was credited with a synergistic combination of cracking (zeolite) and Lewis acid-selective catalysis (ZnCl<sub>2</sub>) (Leng et al., 2013). However, whether it was the Brønsted acid or Lewis acid that played the major role in this catalytic process was not clear. The pyrolysis of corncob impregnated with H<sub>2</sub>SO<sub>4</sub> produced levoglucosenone (LGO) and 1,4:3,6-dianhydro- $\alpha$ -D-glucopyranose

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(DGP) as the main pyrolytic products of cellulose, which could be intermediates for furfural (Branca et al., 2011). This demonstrated that Brønsted acid can be introduced in catalysts for biomass pyrolysis.

In this work, in order to investigate the role of Brønsted acid in biomass pyrolysis, five weak Lewis acid metal sulfates supported on HZSM-5 were selected as catalysts for the pyrolysis of bagasse. The experimental results showed that  $\text{CuSO}_4/\text{HZSM-5}$  was the optimum catalyst for furfural production (28%). But the furfural yields were significantly lower when using HZSM-5 (5%) or  $\text{CuSO}_4$  (4%) alone. The results of pyridine adsorption infrared (Py-IR) spectroscopy of the catalysts showed that  $\text{CuSO}_4/\text{HZSM-5}$  exhibited a stronger Brønsted acid intensity. The Brønsted acid sites appeared to play an important role in promoting the depolymerization of polysaccharides over  $\text{CuSO}_4/\text{HZSM-5}$ .

## 2. Methods

### 2.1. Feed material

The feed material, bagasse, was shattered and screened to obtain 10–80 mesh particles, and then dried in an oven at 105 °C for 48 h.

### 2.2. Catalyst preparation and characterization

The catalysts were prepared via impregnation using an appropriate aqueous solution (deionized water) dissolving a predetermined quantities of metal sulfates (AR, Aladdin). A commercially available HZSM-5 ( $\text{Si}/\text{Al} = 300$ , 320  $\text{m}^2/\text{g}$ , Nankai Catalyst Company, Tianjin, China) was then impregnated with the solution for 24 h. Then the catalyst was dried in an air oven at 40 °C for 24 h then kept at 110 °C for another 12 h.

Infrared spectra of pyridine adsorption (Py-IR) were used to identify the acid site types of the catalysts. About 10 mg of samples were pressed at 10 MPa for 2 min to get a 13 mm wafer. Then the samples were introduced in a situ IR cell and treated at 300 °C in a vacuum for 2 h followed by cooling to room temperature in a vacuum. Subsequently, pyridine was adsorbed for 30 min, and then desorbed at 150 °C for an hour under vacuum. The infrared spectra were collected at 150 °C using a Thermo Nicolet Nexus 6700 FT-IR spectrometer equipped with a liquid nitrogen cooled MCT detector. The Lewis/Brønsted acid (L/B) ratio was calculated as follows:  $\text{L/B} = 1.42\text{IA(L)}/1.88\text{IA(B)}$  (IA(L,B) = integrated absorbance of L or B band) (Emeis, 1993).

### 2.3. Pyrolysis experiments

The pyrolysis experiments were carried out in a tubular quartz packed-bed reactor with a diameter of 25 mm and height of 400 mm which was heated using a resistive electric element. In the middle of the pyrolysis tube, a quartz wool layer was set as a reactant and catalyst support. For each run, a mixture of bagasse (3 g) and catalysts (as a mass ratio) was placed on the support. Prior to heating, a nitrogen carrier gas (60 mL/min) was inlet to purge the reactor system for 15 min. The samples were heated to 500 °C (70 °C/min) and held for 3 min and then cooled to room temperature. The liquid products were collected in a cooled flask connected to the end of the reactor.

The liquid product was analyzed via Shimadzu GC-2014, using an Rtx-5 capillary column (30 m  $\times$  0.32 mm  $\times$  0.25  $\mu\text{m}$ ) and a FID. Oven temperature was held at 40 °C for 5 min and then heated to 280 °C at a rate of 10 °C/min and held at 280 °C for 5 min. The yields of furfural were calculated based on area percentage from GC. The qualitative analysis of the liquid product was carried out

by GC–MS (Agilent GC7890A/MS5975C). The column employed was a HP-5 MS (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ), with helium used as the carrier gas.

## 3. Results and discussion

### 3.1. Screening of the catalysts

To evaluate the performance of the catalysts, a blank test (without catalyst) was conducted as a control. The GC–MS analysis of the liquid products from the control experiment revealed that the components were complex and many furan and pyran compounds were formed but their yields were not high (<3%). The yield of furfural from the control experiment was only 3%. When HZSM-5 was employed, the furfural yield increased to a still unacceptable 5.4%. To improve the furfural yield, a series of metal sulfates ( $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{ZnSO}_4$  and  $\text{CuSO}_4$ ) were investigated in the bagasse pyrolysis. It was found that the product compositions over these metal sulfates were similar to that of non-catalytic test.

Fig. 1 showed furfural yield over various catalysts. All of the metal sulfates showed poor furfural yields (4–6%), nearly equal to the blank test. When the supported sulfates catalysts were employed, the results were interesting and varied.  $\text{Al}_2(\text{SO}_4)_3/\text{HZSM-5}$  (4%) and  $\text{Na}_2\text{SO}_4/\text{HZSM-5}$  (5%) exhibited performance similar to the corresponding single sulfate. However, the  $\text{ZnSO}_4/\text{HZSM-5}$  (10.3%) and  $\text{MgSO}_4/\text{HZSM-5}$  (7.9%) exhibited slightly better catalytic activity than  $\text{ZnSO}_4$  and  $\text{MgSO}_4$ . Surprisingly,  $\text{CuSO}_4/\text{HZSM-5}$  exhibited a particularly good performance with a furfural yield of 28%. Most of the furan and pyran compounds decreased or disappeared leaving furfural as the predominant product. It was proposed that the introduction of  $\text{CuSO}_4$  supported on HZSM-5 intensified the Brønsted acidity, which had a favorable effect on furfural production.

To clarify this proposition, the recycled  $\text{CuSO}_4/\text{HZSM-5}$  catalyst, which was obtained after calcining the residue of char and  $\text{CuSO}_4/\text{HZSM-5}$  at 500 °C in air for 3 h, was investigated. In comparison, the furfural yield using the recycled catalyst was only 9%. It was clear that after coking and calcination there was a loss of Brønsted acid sites in the catalyst (Mores et al., 2007). The decrease of Brønsted acid sites significantly decreased the activity of the catalyst for cracking the biomass to the intermediates for furfural production.

In this work, there was no substantial difference in the distribution of products between each trial. The distribution was as following (by weight): tar (46–52%), char (20–22%) and gas (26–34%).

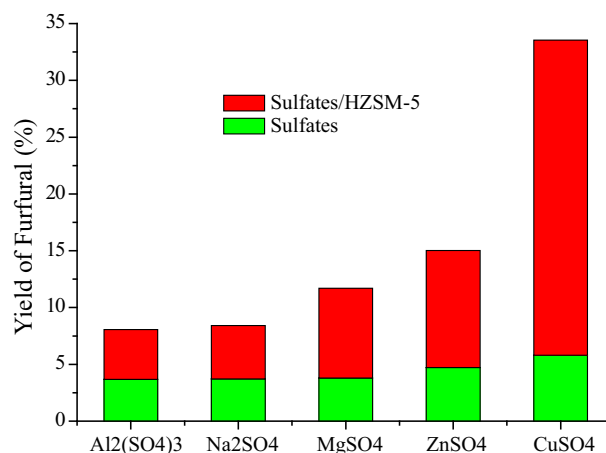


Fig. 1. Yield of furfural under different catalysts.

### 3.2. Optimization experiments

In this work,  $\text{CuSO}_4/\text{HZSM-5}$  was found to be the most effective catalyst. The loading of  $\text{CuSO}_4$  and the dosage of catalyst were further optimized. Fig. 2 (a) showed the influence of  $\text{CuSO}_4$  loadings on the furfural yield. The results showed that the optimum catalyst loading was a mass ratio of 0.4 ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  to HZSM-5). When the ratio was less than 0.4, there were not enough active sites for furfural production. But when it exceeded 0.4, the furfural yield did not improve significantly. Fig. 2 (b) depicted the results for different mass ratios of catalyst to biomass. The results illustrated that increasing amount of  $\text{CuSO}_4/\text{HZSM-5}$  increased the furfural yield. The breaking point was 0.5, because when the ratio exceeded 0.5, little increase of furfural yield was seen.

### 3.3. The relationship between acidity and performance

To identify the relationship between acid types and catalytic performance, the acidity of the catalysts was examined using Py-IR (Fig. 1S). HZSM-5 exhibited two strong bands at  $1446$  and  $1490\text{ cm}^{-1}$  and a weak band at  $1547\text{ cm}^{-1}$ , indicating that both Lewis and Brønsted acidity were found on the surfaces of HZSM-5 and Lewis acid sites were the dominant acid centers ( $\text{L/B} = 42$ ) (Parry, 1963). Interestingly, an increase in Brønsted acid intensity could be clearly observed on  $\text{CuSO}_4/\text{HZSM-5}$  ( $\text{L/B} = 11$ ), which implied that Brønsted acid sites were generated by introducing  $\text{CuSO}_4$  onto HZSM-5. It was speculated that the increase of Brønsted acidity was attributed to the introduction of  $\text{SO}_4^{2-}$ , which may cause a superacid structure to be formed. The Brønsted acid intensity of recycled  $\text{CuSO}_4/\text{HZSM-5}$  ( $\text{L/B} = 63$ ) was weaker than that of the  $\text{CuSO}_4/\text{HZSM-5}$ . Hence, the fact that  $\text{CuSO}_4/\text{HZSM-5}$  exhibited a much better catalytic performance than HZSM-5 and recycled  $\text{CuSO}_4/\text{HZSM-5}$  should be due to the increase in the Brønsted acid intensity. Therefore, Brønsted acid sites played an important role in accelerating polysaccharides depolymerization.

### 3.4. Proposed reaction pathway of biomass pyrolysis over $\text{CuSO}_4/\text{HZSM-5}$

Under heat treatment, both depolymerization and ring scission of polysaccharides will take place. The depolymerization process forms primarily anhydro-oligosaccharides and monomeric anhydrosugars (Lu et al., 2011a,b). Following this, furfural is derived from monomers such as anhydro-xylopyranose, levoglucosan (LG), LGO, DGP and 1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one (LAC) (Shen and Gu, 2009; Shen et al., 2010). The increase in monomers

can result from the depolymerization of anhydro-oligosaccharides. Therefore, an increase in furfural yield implies a decrease in anhydro-oligosaccharides yield. Referring to the Py-IR results, it is the Brønsted acid that promoted the depolymerization of anhydro-oligosaccharides to monomeric anhydrosugars.

Therefore, in biomass pyrolysis, under Lewis acid exposure, although furfural was selectively obtained, it was difficult to completely convert the anhydro-oligosaccharides into monomers. In the presence of the Brønsted acid, more monomers were generated. But the absence of Lewis acid led to a low furfural selectivity. In the presence of both the Brønsted acid and the Lewis acid, the cleavage of glycosidic bonds in anhydro-oligosaccharides and the degradation of monomers into furfural were efficiently executed. Therefore, Brønsted acid had exhibited a significant influence in biomass pyrolysis and surprising improvement in furfural production.

## 4. Conclusion

Five metal sulfates supported on HZSM-5 were evaluated, and  $\text{CuSO}_4/\text{HZSM-5}$  exhibited the best performance in bagasse pyrolysis (28% furfural yield). The optimum reaction conditions called for the mass ratio of  $\text{CuSO}_4/\text{HZSM-5}$  to be 0.4 and the catalyst/biomass mass ratio to be 0.5. The especially high furfural yield of  $\text{CuSO}_4/\text{HZSM-5}$  was attributed to the relatively stronger Brønsted acid intensity compared to HZSM-5 (5%) and recycled  $\text{CuSO}_4/\text{HZSM-5}$  (9%), as identified by Py-IR. According to the reaction pathway of biomass pyrolysis, the presence of Brønsted acid enhanced the depolymerization of anhydro-oligosaccharides to the intermediates, thus resulting in an improvement in furfural production.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2014.07.053>.

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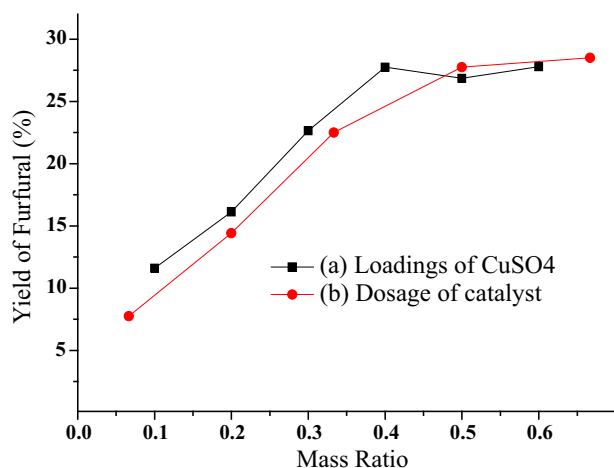


Fig. 2. Optimal conditions for furfural yields over  $\text{CuSO}_4/\text{HZSM-5}$ . Mass ratio of (a)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  to HZSM-5 (b)  $\text{CuSO}_4/\text{HZSM-5}$  to bagasse.

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